

**Valence Band Photoemission from Pt Supported on Cerium Oxide Thin Films**

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**Introduction:** UHV experiments on thin films of cerium oxide have shown that when the ceria is reduced to primarily  $\text{Ce}_2\text{O}_3$  it can alter the adsorption / desorption behavior of CO adsorbed on supported Pt [1]. The adsorption energy of CO is much lower on Pt / Reduced  $\text{CeO}_x$  than on Pt /  $\text{CeO}_2$ . One possible explanation is a modification of the electronic structure of the Pt induced by either charge transfer from the  $\text{CeO}_x$  or a structural change in the Pt particles. We have examined the electronic structure of the Pt and ceria by valence band photoemission. In particular we are looking for variations in the d-band width (so-called d-band broadening), discrete states that might be indicative of charge transfer or bonding with the oxide, and the presence of a Fermi edge which is indicative of metallic vs molecular bonding in the metal cluster. Changes in the oxide density of states may also be indicative of direct interactions between the metal and the oxide.

**Methods and Materials:** The ceria was deposited by evaporating Ce onto Ru(0001) under an  $\text{O}_2$  pressure of  $10^{-8}$  -  $10^{-7}$  torr. The oxidation state of the Ce was controlled by adjusting the  $\text{O}_2$  pressure during Ce deposition. The Pt was then deposited from a resistive metal source. Photoemission spectra were recorded using 115 eV and 150 eV excitation. 150 eV is above the Ce 4d adsorption edge. Spectra at this energy showed an enhancement of the oxide features. Spectra at 115 eV made it easier to see the Pt features.

**Results:** The spectra shown below are from Pt on oxidized (A) and reduced (B) ceria recorded at 115 eV excitation. The spectra are dominated by the O 2p features between 3 – 7 eV. In the spectra from reduced ceria (B), emission from the Ce 4f level is seen near 1.5 eV.

In order to highlight the Pt features, a spectrum from ceria without Pt (**black**) has been subtracted from the spectra with Pt (**red**). The difference spectra are shown in **blue**. The intensity of the clean spectra have been scaled so that the difference spectra show little structure above 6 eV in order to account for attenuation of the oxide by the Pt.

On oxidized  $\text{CeO}_2$  the Pt displays a rise at the Fermi energy indicating metallic Pt and then a broad maximum near 1 eV (A). The remainder of the Pt spectrum is relatively featureless. The spectrum from Pt on reduced  $\text{CeO}_x$  (B) shows more intense Pt features, a discrete peak near 2 eV and a broader Pt d-band.

The d-band broadening is consistent with the weaker CO adsorption energy as proposed by Hammer and Norskov [2]. It isn't clear what causes this d-band broadening. Spectra recorded at 150 eV (not shown) indicate a strong decrease in the Ce 4f intensity compared to the O 2p intensity, perhaps indicating electron transfer from the Ce to the Pt.

Spectra following CO adsorption (not shown) display a strong decrease in Pt intensity near the Fermi edge indicating charge transfer from the Pt to the CO. In addition, CO adsorption eliminates the discrete Pt state near 2 eV on the reduced  $\text{CeO}_x$  substrate.

**Conclusions:** Valence band photoemission from Pt on reduced  $\text{CeO}_x$  shows a more intense and broader d-band structure compared to Pt on oxidized  $\text{CeO}_2$ . This difference in the electronic structure correlates with a weaker CO adsorption energy on Pt /  $\text{CeO}_x$ .

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**References:**

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- [2] B. Hammer and J. K. Norskov, *Adv. Catal.* 45 (2000) 71.

